Chapter 9
Cross-Media Interpretations

9.1 Summary of Mercury Concentrations in Lake Michigan Compartments

Mercury was found throughout the Lake Michigan ecosystem, with concentrations measured in air, water, sediment, tributaries, plankton, and fish samples collected from in and around the lake. Mercury was found in the majority of samples at levels above the corresponding detection limit for each ecosystem compartment (Table 9-1). Other than one sediment sample and one plankton sample, total mercury was detected in every sample in all media other than the open-lake water column. A total of 8 particulate mercury samples and 4 total mercury samples in the open-lake water column did not contain detectable levels of mercury. Comparisons of these frequencies should be done with care, due to the different types of detection limits used in the different mercury data sets. The type of detection limit used for the atmospheric phase or analytical fraction was described by the PI responsible for the analyses. Samples were only analyzed for methylmercury in the tributary compartment, and methylmercury was detected at levels above the MDL for the majority of the tributary samples. Approximately 15% and 3% of the dissolved and total samples, respectively, did not have detectable levels of methylmercury.

Table 9-1. Summary of Samples from each Ecosystem Compartment with Detectable Levels of Mercury

Ecosystem Compartment	Atmospheric Phase or Analytical Fraction	Detection Limit Type	% Samples with Mercury Above Detection Limit
Atmosphere	Vapor	System Detection Limit	100%
	Particulate	System Detection Limit	100%
	Precipitation	Method Detection Limit	100%
Tributary	Dissolved	Method Detection Limit	100%
	Total	Method Detection Limit	100%
Tributary Methylmercury	Dissolved	Method Detection Limit	85%
	Total	Method Detection Limit	97%
Open Lake	Particulate	Daily Detection Limit	92%
	Total	Daily Detection Limit	96%
Sediment	Total	Sample-Specific Detection Limit	99.5%
Plankton	Total	Sample-Specific Detection Limit	99%
Fish	Total	Method Detection Limit	100%

Vapor-phase mercury concentrations averaged from 2.06 to 3.62 ng/m^3 at five different shoreline and out-of-basin stations. The highest concentrations of vapor-phase mercury were detected at the IIT Chicago station, at the southern end of Lake Michigan. Particulate-phase mercury concentrations were lower than vapor-phase concentrations, with means ranging from 12.1 pg/m^3 to 73.7 pg/m^3. At individual stations, the mean vapor-phase concentration was 49 to 175% greater than the mean particulate-phase concentration. As with the vapor phase, the higher particulate-phase mercury concentrations were found at the IIT-Chicago site. Mean precipitation-phase mercury concentrations ranged from 15.2 to 26.1 ng/L. When calculated by weighting the concentrations according to the sample volume, mean precipitation-phase mercury concentrations ranged from 11.0 to 21.1 ng/L. As with the other two atmospheric phases, the highest mean concentration in the precipitation phase was measured at the IIT Chicago station.

Total mercury concentrations in Lake Michigan tributaries averaged from 1.07 to 28.9 ng/L, and dissolved mercury concentrations averaged from 0.666 to 3.71 ng/L. When calculated using the

differences between total mercury and dissolved mercury concentrations in individual samples, mean particulate mercury concentrations averaged from -0.0058 to 25.8 ng/L. In all cases, the highest mean concentrations were measured in the Fox River, a tributary that empties into Green Bay. The Fox River watershed is highly industrialized, and is suspected of being impacted by resuspension of contaminated sediments from legacy sources (Hurley *et al.*, 1998a; Rossmann and Edgington, 2000). Generally, among the other tributaries, mercury levels were higher in more urban/industrialized areas, and lower in primarily agricultural/forested areas.

Within the open-lake water column, total mercury concentrations averaged from 0.25 to 0.78 ng/L, and particulate mercury concentrations averaged from 0.029 to 0.17 ng/L. Generally, mercury was well mixed in the water column, as there was little variability in concentration among stations. While there was a slightly greater concentration of particulate mercury in Green Bay, there was no corresponding increase of total mercury.

The mean mercury concentration measured in precipitation samples was approximately 2.6 times greater than the mean total mercury concentration measured in the tributaries. With the exception of the Fox River tributary, all mean precipitation-phase mercury concentrations were greater than the mean total mercury concentration at any tributary. The mean mercury concentration in the Fox River was greater than the mean concentration in precipitation at any of the atmospheric stations. The overall mean precipitation-phase and tributary concentrations were 64 and 24 times greater than the mean total mercury concentration in the water column, respectively.

Total mercury concentrations measured in surficial sediments ranged from 0.002 to 0.26 mg/kg. Higher levels of mercury tended to accumulate in the sediments in deeper locations of the lake. Net fluxes of mercury ranged from 0.85 to 21 ng/cm^2/y and were highest along the eastern shore in response to the dominant water currents in the lake. Additional samples were collected from five different sediment trap stations, including two which were set at two different depths. Mean mercury concentrations for the different trap stations and depths ranged from 0.21 to 28 mg/kg. The highest mercury concentrations were found in samples collected from traps located in the southern basin of Lake Michigan. Both mercury concentrations and fluxes to surficial sediments have decreased since the 1970s.

9.2 Mercury Speciation

As discussed in Section 2.1.6 of this report, the organic compounds methylmercury and dimethylmercury have a greater toxicity than inorganic mercury, given equivalent doses. Methylmercury is generally the dominant form of mercury in higher levels of the aquatic food web. Methylmercury usually forms through methylation of inorganic mercury by bacteria in sediments or in the water column. Therefore, although atmospheric deposition and tributary flows are major sources of inorganic mercury to the lake, they may not be major sources of methylmercury.

Among the ecosystem components in Lake Michigan from which mercury samples were collected, methylmercury samples were collected from only the tributary component. While total mercury levels were greatest from the Fox River, and other tributaries located near urban/industrial sources, this was not the case for methylmercury. Tributaries located in mostly agricultural and forested areas such as the Menominee and Muskegon rivers had among the highest methylmercury concentrations. The Grand Calumet River, which had one of the highest mean total mercury concentrations and is located near the Chicago/Gary urban area, had the lowest mean methylmercury concentration.

The relative contribution of methylmercury to the total mercury concentrations measured in the tributaries was evaluated by calculating the percentage of the mean methylmercury concentration to the mean total

mercury concentration in each tributary. The percentage of mean methylmercury concentration to mean total mercury concentration ranged from 0.48% to 21% in the 11 tributaries. The 21% figure was for the Muskegon River, and the percentage contributions for the other 10 tributaries were all less than 6%. These lower percentages are consistent with other estimates of the contribution of methylmercury to total mercury in the water column (USEPA, 1997b), which indicate that methylmercury constitutes less than 10% of the total mercury concentration in water samples.

The percentage of methylmercury is greater in plankton and fish than in water samples. For example, Watras and Bloom (1992) measured both methylmercury and total mercury in various trophic levels in a basin of the Little Rock Lake, Wisconsin. Little Rock Lake is in north-central Wisconsin, in a relatively remote area with no industrial activity, and with restricted public-access. The lake is fed by groundwater and is used as an experimental lake. The lake has been artificially divided into two basins, one of which is acidified relative to the rest of the lake.

Watras and Bloom (1992) found that the percentage of methylmercury to total mercury in the water column and biota varied with pH as shown in Table 9-2, below.

Table 9-2. Percent of Mercury Attributable to Methylmercury in Little Rock Lake

	% Methylmercury of the Total Mercury	
Ecosystem Component	Reference Basin (pH = 6.1)	Acidified Basin (pH = 4.7)
Water column	5	12
Phytoplankton	13	31
Zooplankton	29	91
Fish	>90	>90

Both basins of the experimental lake were acidic, with a pH of 4.7 in the acidified basin, and 6.1 in the reference basin. In contrast, the mean pH measured in Lake Michigan for the LMMB Study was 8.2. Mason and Sullivan (1997) and Sullivan and Mason (1998) reported methylmercury concentrations in Lake Michigan that ranged from the detection limit of 5 pg/L to 42 pg/L, with an epilimnetic mean of 6 pg/L for August 1994 and 8.2 for October/November of 1994. (When calculating the mean, the detection limit of 5 pg/L was substituted for any sample result below the detection limit.) The hypolimnetic mean for August 1994 was 8 pg/L; whereas, the hypolimnetic concentrations for two samples in October/ November 1994 were 17 and 42 pg/L. These concentrations represent 2-3% of the mean total mercury concentration (Sullivan and Mason, 1998), which are lower than those reported by Watras and Bloom (1992).

A subsequent study of small lakes in northern Wisconsin by Watras *et al.* (1998) included the two basins of Little Rock Lake and 13 others lakes. The majority of these lakes are precipitation-domination seepage lakes in which the flows are dominated by precipitation, rather than riverine flow. Watras *et al.* (1998) measured the concentrations of total mercury, dissolved mercury, total methylmercury, and dissolved methylmercury in samples of dissolved organic carbon (DOC), microseston, zooplankton, and small fish. The microseston in the lakes in that study primarily consists of phytoplankton, bacterioplankton, and cellular debris. The zooplankton were collected in 153-μm mesh nets (a slightly larger mesh than used in the LMMB Study). It total, 727 yellow perch (*Perca flavescens*) and 139 golden shiners (*Notemigonus crysoleucas*) were collected during the spring and summer of 1994, ranging from one to seven years in age. Total mercury and total methylmercury were also measured in surficial sediments collected from these lakes.

Watras *et al.* (1998) reported the percentage of methylmercury relative to the total mercury concentration in the DOC, microseston, zooplankton, and small fish, as shown in Table 9-3. The mean pH of the lakes

on the study was 6.25, slightly higher than the reference basin in Little Rock Lake, and still well below the mean pH of 8.2 in the LMMB Study.

Table 9-3. Percent of Mercury Attributable to Methylmercury in 15 Lakes in Northern Wisconsin

Ecosystem Component	% Methylmercury of the Total Mercury
Dissolved organic carbon	11%
Microseston (includes phytoplankton)	18%
Zooplankton	57%
Fish	95%

Except for the fish, the percentages of methylmercury in Table 9-3 are intermediate to the results for the two basins on Little Rock Lake shown in Table 9-2. The results for the fish are comparable to those in Table 9-2, where the fish are listed as ">90%."

There has been one report of methylmercury in Lake Michigan sediments. Rossmann *et al.* (2001) reported methylmercury results for surficial sediments samples from Lake Michigan that were originally collected in 1994 - 1996 as part of the LMMB, but not analyzed for methylmercury as part of this study. The methylmercury concentrations ranged between 0.16 and 1.7 ng/g, with a mean and median of 0.57 and 0.45 ng/g, respectively. The methylmercury concentration varied between 0.11 and 1.4% of the total mercury concentration. The mean and median fraction of methylmercury were 0.42 and 0.35%, respectively.

The results from Watras *et al.* (1998) for methylmercury in surficial sediments of the lakes in northen Wisconsin are slightly higher than those from Rossmann *et al.* (2001), with a range of 0.5 to 7.4 ng/g, with a mean of 2.6 ng/g. The methylmercury concentration varied between 0.5 and 3.9% of the total mercury concentration, with a mean fraction of methylmercury of 1.5%.

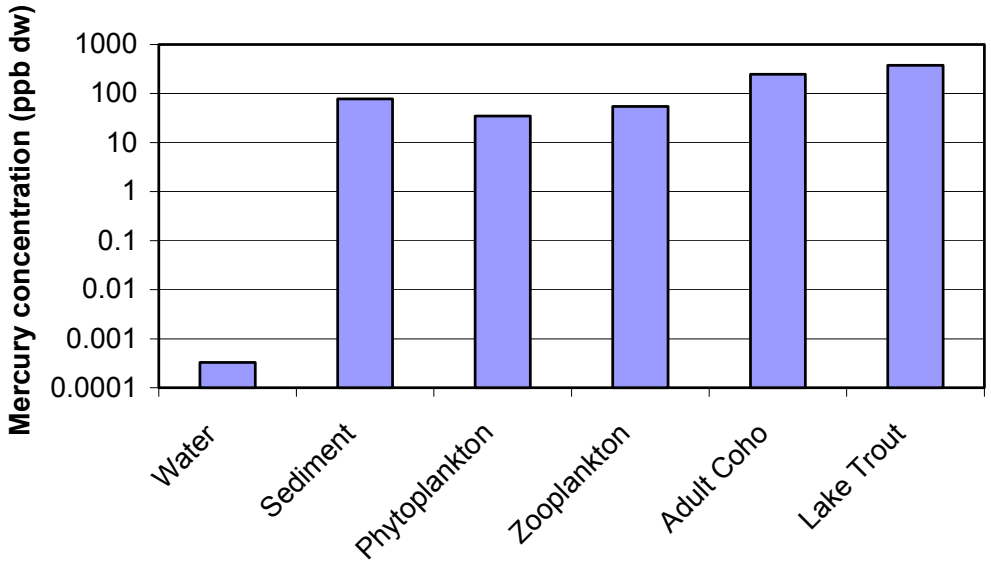
Studies comparing methylmercury and total mercury levels in fish have consistently shown that the majority of the measured total mercury consists of methylmercury. Herrin *et al.* (1998) measured mercury in bluegill and shiners in Devil's Lake, Wisconsin, and found that methylmercury accounted for nearly all of the total mercury in both species. However, they also found that methylmercury accounted for 26% to 58% of total mercury in open water, higher than most estimates. Rossmann *et al.* (2003) reported mean total and methylmercury concentrations in forage fish to be 0.051 and 0.34 mg/kg, respectively with methylmercury concentrations accounting for 60 and 91% of the total mercury for various species. Francis *et al.* (1998) also measured methylmercury and total mercury in various fish species in an estuary of Lake Erie. While mercury concentrations were frequently below detection limits, the percentages attributable to methylmercury were usually greater than 90% in common carp and channel catfish.

Unlike the two studies described above, Cappon (1984) measured methylmercury and total mercury in lake trout and coho salmon in Lake Ontario, allowing greater comparability with the LMMB Study. On average, methylmercury accounted for 71% of total mercury in both lake trout and coho salmon, a much lower percentage than those observed in the other studies. The levels of total mercury in lake trout in Lake Ontario were slightly higher, with a mean of approximately 165 ng/g on a wet-weight basis, compared to 139 ng/g in the LMMB Study. The levels of total mercury in Lake Ontario, however, were much higher, with a mean of approximately 240 ng/g, compared to 69 ng/g in the LMMB Study. Therefore, it is unclear whether the percentages of methylmercury from the study in Lake Ontario were unusually low due to taxonomic differences, or due to unusually high total mercury results.

9.3 Bioaccumulation and Biomagnification

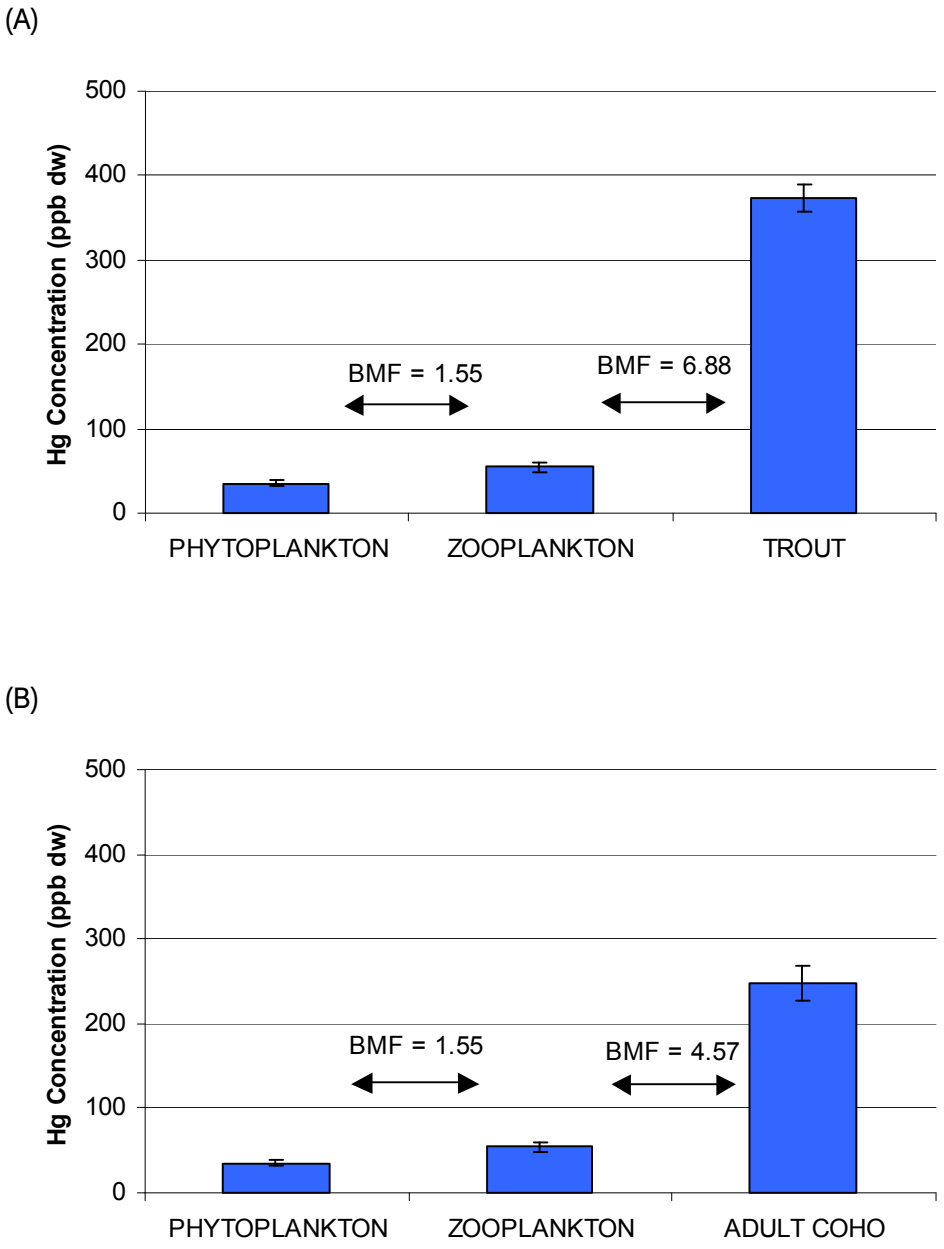
Mean mercury concentrations in the biota and mean concentrations in the water column and surficial sediments are presented in Figure 9-1. Within living components of the Lake Michigan ecosystem, mercury accumulated at concentrations higher than in any abiotic ecosystem component, with the exception of surficial sediments. Bioaccumulation factors for mercury ranged from 1.1×10^5 in phytoplankton to 1.1×10^6 in lake trout.

Figure 9-1. Mercury Concentrations in Various Components of the Lake Michigan Ecosystem



In addition to accumulating in living tissue at concentrations above those in the water, mercury also was magnified within the Lake Michigan food web (Figure 9-2). Total mercury concentrations increased from 35 ng/g in phytoplankton to 55 ng/g in zooplankton, a factor of 1.55. While samples of forage fish were not initially analyzed for mercury in the LMMB, an approximate two-step biomagnification factor can be calculated between zooplankton and the predator fish. The mean dry-weight mercury concentration in adult coho was 248 ng/g, and the mean mercury concentration in lake trout in adult coho was 373 ng/g. These concentrations correspond to biomagnification factors of 4.57 and 6.88, compared to zooplankton, respectively. From the bottom of the food web (phytoplankton) to the top of the food web (lake trout), mercury concentrations increase by a factor of 10.7.

Figure 9-2. Biomagnification Factors for Mercury in Lake Trout (A) and Adult Coho (B)



Because forage fish samples were not analyzed for mercury, biomagnification of mercury in the upper pelagic food web could not be estimated and compared to that calculated in total PCBs and *trans*-nonachlor (USEPA, 2003). However, biomagnification factors between zooplankton and predator fish species were much lower than those calculated for PCBs and *trans*-nonachlor. For total PCBs the biomagnification factor between zooplankton and *Mysis* was 1.5, and the factor between *Mysis* and lake trout was 31, yielding an estimated factor of 46.5 between zooplankton and lake trout. Similarly, the biomagnification factor between zooplankton and *Mysis* for *trans*-nonachlor was 1.6 and the factor between *Mysis* and lake trout was 19, yielding an estimated factor of 30.4 between zooplankton and lake trout. These factors were much larger than the corresponding factor of 6.88 for mercury. The biomagnification factor between phytoplankton and zooplankton was also smaller for mercury, at 1.55, compared to 3.4 for total PCBs and 9.5 for *trans*-Nonachlor.

The biomagnification of mercury in Lake Michigan occurred at a higher rate compared to previous studies in other lakes. For example, Herrin *et al.* (1998) measured a biomagnification factor for mercury of 2.7 between *Daphnia* and bluegills in Devil's Lake, Wisconsin in 1994 and 1995. The mean dry-weight total mercury concentrations measured in bluegills in Devil's Lake were 575 ng/g in 1994 and 324 ng/g in 1995. These levels are comparable with the mean of 373 ng/g measured in Lake Michigan in this study. The smaller biomagnification factor from Devil's Lake was likely due to greater mercury concentrations in the *Daphnia* compared to the zooplankton in Lake Michigan and the fact that bluegills are a step lower in the food chain than lake trout.

While mean total mercury concentrations were not reported for *Daphnia* in Devil's Lake, the mean methylmercury concentrations of 186 and 100 ng/g in 1994 and 1995 were 3.38 and 1.82 times greater than the mean total mercury concentration in zooplankton in Lake Michigan. The open-water total mercury concentrations were also greater in Devil's Lake, with a mean of 3.0 ng/L total mercury, almost an order of magnitude greater than the mean concentration observed in Lake Michigan. In addition, the biomagnification factors calculated in Devil's Lake were based on methylmercury, not total mercury. While the total mercury and methylmercury levels were comparable in that study, total mercury levels may have been considerably greater in *Daphnia* than the measured methylmercury concentrations, which would yield a biomagnification factor which would be greater than one calculated based on total mercury. For example, Watras and Bloom (1992) found that 29% of zooplankton mercury in Little Rock Lake, WI was methylmercury; whereas >90% of total mercury measured in fish was methylmercury. The comparability of the two studies may also be affected by the taxonomic differences of the sampled fish. Bluegills tend to be smaller than trout and will likely be lower on the food web than lake trout. In an EPA survey of mercury concentrations of fish (USEPA, 1999b), bluegills were found to have lower concentrations than most other fish species from which samples were collected, including largemouth bass, walleye and northern pike. Bluegill caught in Wisconsin for this survey had comparable mercury concentrations to those measured in Devil's Lake.

Francis *et al.* (1998) also found evidence of mercury biomagnification in Old Woman Creek, an estuary of Lake Erie. However, bioaccumulation and biomagnification factors could not be calculated, due to the prevalence of open-water, plankton, and fish samples without detectable levels of mercury. The detection limits reported in that study were higher than those for the LMMB Study, by up to two orders of magnitude in water and fish tissue samples. While mercury was also not detected in zooplankton samples, the detection limits for plankton samples in the two studies were comparable. However, the authors did conclude that bioaccumulation was occurring, based on higher levels of mercury, and greater rates of detection, in predatory catfish and bowfin.